

**Title:** Field and Laboratory Validation of Photoactivated Adsorption for Removal of Arsenic in Groundwaters

**Project I.D.:** DNR Project #179; NMD00000240

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**Period of Contract:** *Begin Date* – July 1, 2003; *End Date* – June 30, 2004

**Background/Need:** The EPA has lowered the maximum contaminant level (MCL) for arsenic in drinking water from 50 ppb to 10 ppb, effective in 2006. Many treatment facilities must implement additional technologies to meet this revised MCL. Because the associated costs will be extremely burdensome for small communities, numerous studies are targeted at developing more cost-effective treatment technologies for arsenic removal by municipalities and in homes than are available at present.

**Objectives:** The main objective of this study is to validate new technologies for arsenic treatment that are being developed in our laboratory. These technologies involve 1) preparing more effective adsorbents for removing arsenate (a form of arsenic that is relatively easy to treat) from water and 2) testing photocatalytic oxidation as a method for converting arsenite (a form of arsenic that is difficult to remove from water) to arsenate. Five tasks were designed to satisfy the main objective.

**Methods:** **Task 1:** Characterize the adsorption chemistry of arsenate on a commercial activated alumina, including the effect of the presence of other species. Batch studies were conducted to determine the adsorption density of arsenate on AA-400G (Alcan Chemical) as a function of zeta potential, system pH, arsenate concentration, and the concentrations of silicate, sulfate, and magnesium. **Task 2:** Optimize a material to photooxidize arsenite and adsorb the arsenate produced by photooxidation. Several studies were performed by passing test solutions through columns packed with glass rings coated with titania photocatalyst and illuminated by near-UV fluorescent bulbs. These studies elucidated the effects of dissolved oxygen concentration, adsorption of photogenerated arsenate, and the use of a natural water on the rate of arsenite photooxidation. **Task 3:** Develop methods for coating these materials on substrates for use in photoreactors. Spray coating was evaluated for this purpose. **Task 4:** Field test these technologies in a small community. A bench scale photoreactor was tested at Danvers, IL for its ability to convert arsenite to arsenate in a natural water. However, this reactor was not designed to remove photogenerated arsenate. **Task 5:** Perform a cost-benefit analysis for using these technologies. This task was not completed because of constraints associated with the field test.

**Results and Discussion:** **Task 1:** Adsorption densities for arsenate decreased in the presence of silicate and sulfate but increased with added magnesium. Although sulfate does not appear to compete directly with arsenate for adsorption sites, the surface charge of alumina is

affected by the concentration of sulfate, which in turn affects the adsorption of sulfate and makes this process highly pH dependent. On the other hand, arsenate and silicate both bond chemically to alumina and compete directly for adsorption sites. This process is less dependent on pH than for sulfate competition. Dissolved magnesium actually increases the adsorption of arsenate at a given pH. **Task 2:** Arsenite photooxidation requires at least a similar concentration of dissolved oxygen. The rate of photooxidation is not affected by adsorption of photogenerated arsenate but can decrease when natural waters are treated. **Task 3:** Spray coating can be employed to deposit photocatalysts on suitable supports and appears to be readily scalable for industrial applications. **Task 4:** A bench scale photoreactor is able to photooxidize arsenite using feed water available at a water treatment facility. The water must have some dissolved oxygen present, and the preference is to use water that has been pretreated to remove dissolved iron so as to prevent deposition of iron oxides on the photocatalyst. Over the four different contact times used for this test, photooxidation of arsenite adhered reasonably well to a second-order kinetic expression ( $r^2 = 0.945$ ). **Task 5:** Because the photoreactor employed for the field test was extremely light limited and because the removal of arsenate was not evaluated, a cost-benefit analysis was not undertaken at this time.

**Conclusions/  
Implications/**

**Recommendations:** **1)** To predict the effectiveness of an adsorbent for removing arsenate, the natural water under study must be well-characterized as changes in water composition may change the effectiveness of an adsorbent. Because dissolved magnesium increases the adsorption capacity of activated alumina for arsenate, further study of the effect of water hardness on arsenic treatment is warranted. **2)** Photocatalytic oxidation can convert arsenite to the more-readily-treatable arsenate if the water contains some dissolved oxygen. Applications of this technology will require pretreatment of the water to minimize precipitation of iron and manganese oxides on the photocatalyst. Designers should consider using waveguide photoreactors in which the photocatalyst is deposited on flat surfaces such as plastics that can direct light throughout the reactor. For these designs, spray coating the photocatalyst on the flat substrate appears to be easily scalable for commercial use. **3)** Additional study is needed to determine if a single reactor using a combination adsorbent/photocatalyst is more cost-effective than a two-stage reactor that separates these processes.

**Related**

**Publications:** The first two tasks are discussed in Eunkyoo Lee, Effects of pH and competitive adsorption of anions on the uptake of arsenate onto activated alumina and the  $\text{TiO}_2$  photocatalytic oxidation/adsorption of arsenite, Ph.D. Thesis, University of Wisconsin – Madison, 2004. A publication on competitive adsorption of arsenic and sulfate is being revised after initial submission to *Water Research*. A second paper on a field test of photocatalytic oxidation of arsenite is in preparation.

**Key Words:** Arsenic; Arsenite; Arsenate; Adsorption; Oxidation; Photocatalytic Oxidation

**Funding:** State of Wisconsin Department of Natural Resources

**Final Report:** A final report containing more detailed information on this project is available for loan at the Water Resources Institute Library, University of Wisconsin - Madison, 1975 Willow Drive, Madison, Wisconsin 53706 (608) 262-3069.